Decreasing DOC trends in soil solution along the hill slopes at two IM sites in southern Sweden – geochemical modeling of organic matter solubility during acidification recovery.

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Abstract

Numerous studies report increased concentrations of dissolved organic carbon (DOC) during the last two decades in boreal lakes and streams in Europe and North America. Recently, a hypothesis was presented on how various spatial and temporal factors affect the DOC dynamics. It was concluded that declining sulphur deposition and thereby increased DOC solubility, is the most important driver for the long-term DOC concentration trends in surface waters. If this recovery hypothesis is correct, the DOC levels should increase both in the soil solution as well as in the surrounding surface waters as soil pH rises and the ionic strength decline due to the reduced input of SO_4^{2-} ions. In this project a geochemical model was set up to calculate the net humic charge and DOC solubility trends in soils during the period 1996-2007 at two integrated monitoring sites in southern Sweden, showing clear signs of acidification recovery. The Stockholm Humic Model was used to investigate whether the observed DOC solubility is related to the humic charge and to examine how pH and ionic strength influence it. Soil water data from recharge and discharge areas, covering both podzols and riparian soils, were used. The model exercise showed that the increased net charge following the pH increase was in many cases counteracted by a decreased ionic strength, which acted to decrease the net charge and hence the DOC solubility. Thus, the recovery from acidification does not necessarily have to generate increasing DOC trends in soil solution. Depending on changes in pH, ionic strength and soil Al pools, the trends might be positive, negative or indifferent. Due to the high hydraulic connectivity with the streams, the explanations to the DOC-trends in surface waters should be searched for in discharge areas and peatlands.

1. Introduction

Numerous studies report increased concentrations of dissolved organic carbon (DOC) during the last two decades in boreal lakes and streams in Europe, Canada and the US (Erlandsson et al., 2008 ; Evans et al., 2005; Monteith et al., 2007; Skjelkvåle et al., 2005). Many different processes have been proposed to explain these trends e.g. hydrometeorological conditions (Erlandsson et al., 2008; Sarkkola et al., 2009), recovery from acidification due to reduced sulphur deposition (Dawson et al., 2009; Monteith et al., 2007), land cover (Laudon et al., 2009; Sarkkola et al., 2009), forest management and land use (Laudon et al., 2009; Löfgren et al., 2009b; Yallop and Clutterbuck, 2009) etc. Recently, Clark et al. (2010) presented a unifying hypothesis on how various spatial and temporal factors affect the DOC dynamics. They concluded that declining sulphur deposition and thereby increased DOC solubility, is the most important driver for the long-term DOC concentration trends in surface waters, but that the variability between sites is influenced by a multitude of spatial and temporal factors (op. cit.).

Soils and surface waters in the historically most polluted southern Sweden show clear signs of recovery from acidification since the early 1990's (Karltun et al., 2003; Löfgren et al., 2009a; Skjelkvåle et al., 2005). However, if the recovery hypothesis is correct, the DOC levels should increase both in the soil solution as well as in the surrounding surface waters as soil pH rises and the ionic strength decline due to the reduced input of SO_4^{2-} ions. In contrast to surface waters, however, the soil waters in forested recharge areas (number of monitoring sites (n_{sites}) =68, 50 cm soil depth, podzols) exhibit no change (n_{sites}=32) or decreasing (n_{sites}=31) DOC concentrations during the period 1986-2008 in southern Sweden, indicating increased coagulation of DOC in the upper soil horizon (Zetterberg and Löfgren, 2009, Löfgren and Zetterberg in prep.). In Norway, similar results were obtained, with no change or decreasing DOC trends during the period 1996-2006 in soil water (n_{sites}=18) at 15 and 40 cm soil depth in podzols (Wu et al., 2010). In contrast, increased DOC concentrations were found in soil water at two sites during the period 1994-2007 in the Czech Republic. The latter studies represent soil water under the forest floor at Lysina and in the mineral topsoil at Pluhuv (Hruska et al., 2009). Positive

DOC-trends were also found at 5-20 cm soil depth (n_{sites}=9, moorlands and forests) during the period 2000-2005 in the UK (Buckingham et al., 2008).

Hruska et al. (2009) concluded that the DOC trends in both soil and surface waters were explained by changes in ionic strength, rather than acidity, while Buckingham et al. (2008) considered the UK time series too short, for making a coupling to the surface water DOC trends. Wu et al. (2010) proposed that small changes in the atmospheric deposition during the investigation period could explain the diverging DOC trends in soil and surface waters. However, they also put forward the possibility of competition between mineral anions and DOC for adsorption sites on oxide surfaces, causing a simultaneous decrease of the DOC and SO_4^{2-} concentrations. Zetterberg and Löfgren (2009) hypothesized that processes in discharge areas and peat lands rather than dry soils uphill govern the surface water DOC trends.

The solubility of DOC is likely to be determined by a number of different biological, chemical and hydrological processes (see Clark et al., 2010 and references therein), but the acidification recovery theory is primarily coupled to the chemical and physical properties of organic matter in soils and water. According to classical DLVO theory for colloidal stability, the surface potential of a charged colloid may be the single most important factor determining its dispersion into the water phase (e.g. Weng et al., 2002). A high surface potential results in more interactions with water molecules and thus a high water solubility. Therefore, different models have been forwarded that relates the DOC solubility either to the surface potential or to the net charge, which is closely related to the surface potential.

Tipping and Woof (1990) suggested a model for DOC dissolution from soils that assume a nonlinear relationship between the DOC concentration and the net humic charge. According to this model, an increased net charge leads to an increasing DOC concentration. The net charge is calculated using an advanced geochemical model that accounts for the acid-base and metal complexation properties of the organic matter, such as WHAM (Tipping and Woof, op. cit.), NICA-Donnan (Weng et al., 2002) or SHM

(Stockholm Humic Model; Gustafsson, 2001). The model of Tipping and Woof (1990) was slightly modified by Lofts et al. (2001) for the WHAM model and by Lumsdon (2004) for the NICA-Donnan model, and after optimization for individual soils it was found to work well in most cases for predicting the DOC concentration, although difficulties were observed in particular for some mineral soils (c.f. the Discussion section).

A slightly different approach was taken by Weng et al. (2002) who instead related the DOC solubility to the value of a Donnan potential calculated by the NICA-Donnan model, assuming that the Donnan potential was closely related to the surface potential of the humic colloids. These authors found that the magnitude of DOC solubility was related to the Donnan potential in five of six soils, but that acid sandy soils seemed to deviate from the general rule.

If the DOC concentration is related to the net humic charge, it may provide a tool to understand why the DOC concentrations show no trend or decrease in Swedish soil waters simultaneously with acidification recovery.

The aim of this project was to set up a geochemical model to calculate the development of the net humic charge with time at the Swedish integrated monitoring (IM) sites Aneboda and Kindla, to investigate whether the observed DOC solubility in soils is closely related to the humic charge, and if so, use the model to examine the factors influencing the humic charge and thus the DOC solubility. The SHM model was tested on soil water data from one transect along the hill slope in each catchment, covering the time period 1996-2007. The transects extend from recharge to discharge areas, making it possible to estimate the net humic charge in both podzols and riparian soils.

2. Site descriptions

Locations and maps of the IM sites Aneboda (19.6 ha, N57°05', E14°32') and Kindla (19.1 ha, N59°45', E14°54') are shown in Figures 1 and 2, respectively. Both sites are

protected Norway spruce (*Picea abies*) forests, not affected by forestry during the last century (Lundin et al., 2001). The bedrock consists of granite and glacial till is the dominant parent material with quartz and feldspar (albite, plagiclase, microcline) as the most abundant minerals. At Aneboda, the annual mean temperature is 5.8°C, precipitation 750 mm and runoff 280 mm. At Kindla, the same figures are 4.2°C, 900 mm and 450 mm respectively. Between 1996 and 2008, the S-deposition in throughfall has diminished from 6 to 2 kg S ha^{-1} y^{-1} at both sites, while the bulk deposition reductions are from 4 to 3 kg S ha^{-1} y^{-1} at Aneboda and from 4 to 2 kg S ha^{-1} y^{-1} at Kindla. In the late 1980's, the S deposition was more than twice these levels (Westling and Lövblad, 2000). Since 1996, the bulk deposition of inorganic N has diminished with ca 1 kg N ha^{-1} y^{-1} and is at present approximately 7 and 5 kg N ha^{-1} y^{-1} at Anaboda and Kindla, respectively. Compared with the S deposition in the historically, heavily polluted Czech Republic (Lysina and Pluhov Bor), which has experienced total S deposition reductions from 30-40 kg $ha^{-1}yr^{-1}$ to 7-11 kg $ha^{-1}yr^{-1}$ during the 1990's (Hruska et al., 2009), the S deposition at the Swedish sites are low. Regarding N deposition, the differences are much smaller and at present a couple of kg N $ha^{-1}yr^{-1}$ higher at the Czech sites. At Aneboda, the throughfall of chloride exhibits large between year variations, with the highest loads in 1999 (20 kg Cl ha^{-1} y^{-1}) and the lowest in 2005 (7 kg Cl ha^{-1} y^{-1}), respectively. At Kindla, the interannual variation is less or 7-12 kg Cl ha^{-1} y^{-1}.

Figure 1

Figure 2

3. Methods

The soil and surface water sampling is part of the ordinary IM-program (Lundin et al., 2001, http://www.environment.fi/default.asp?node=6329&lan=en). Since 1996, stream water is sampled biweekly at each catchment outlet (Figure 2). In both catchments, lysimeters (ceramic cups P80, 1 μm cut-off) were installed along a hillslope in 1994 (Figure 2). In the Aneboda transect, the lysimeters were installed at distances of approximately 1-6 m and 20 m from the stream. Additionally, a group of lysimeters was

established 90-110 m from the stream close to the intensive soil and vegetation plots (Figure 2). In the Kindla transect, the distances to the stream were 4-8 m, 20 m and 40 m (Table 1). In recharge areas and intermediate zones (recharge area except for at runoff events with high groundwater levels) with podzols, the lysimeters were installed in the mineral soil just below the O-horizon (E-horizon) and in the centre of the B-horizon. The E- and B-horizon lysimeters were installed pair wise, within a distance of <1m. Multiple such lysimeter pairs were installed within a distance of <6m from each other at each location along the transects (and plot). In the discharge areas, the lysimeters were installed in the peat-covered gleysols and histosols (30 cm and 37 cm, respectively) below soil surface. Soil temperature, measured by termistors (Aanderaa, 30 minutes interval), is available from 10, 32, 44 and 58 cm and 5, 10, 20 and 35 cm soil depths at Aneboda and Kindla, respectively. Soil water has been sampled since 1994, but in order to minimize installation effects on the time series, this study includes data only from the period 1996-2007. If available, soil water was collected 3-4 times per year after snowmelt (April-May) and precipitation events in August and October-November. At Aneboda, few data are available from the E-horizons due to dry conditions in the surface soils. Therefore, the E-horizon data is omitted from this study. The transects cannot be considered as representative for the mosaic of hillslope conditions creating the stream water chemistry, but are rather examples of such conditions.

The samples were analyzed with Swedish standard methods at the Dept. of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU). The analytical methods are accredited by SWEDAC (Swedish Board for Accreditation and Conformity Assessment). Ambient pH was analysed in a semi-closed system. Directly after opening the bottle, the sample was pumped (peristaltic pump) through an airtight cuvette equipped with a combination pH-electrode adapted for low ionic strength waters (Metrohm 6.0253.100). Samples for total organic carbon (TOC) analysis were measured using a Shimatzu TOC 5050 analyzer with ASI-502 sample injector following acidification. Major cations, Fe and Al were analyzed on acidified samples (0.5 ml concentrated HNO_3 per 100 ml sample) by ICP-OES (Varian Vista Ax Pro) and strong

acid anions by ion chromatography (LDC Conducto Monitor III). Acid neutralizing capacity (ANC) was calculated according to Reuss and Johnson (1986).

The non-parametric Seasonal Kendall test (Hirsch and Slack, 1984; Loftis et al., 1991) was used for detecting monotonous trends in measured and simulated (see below) chemical time series. It was visually determined whether the trends were monotonous or not. Thiels slope (Helsel and Hirsch, 1992) was used to quantitatively estimate the trends. Throughout the investigation period soil water data were available only from the months April-May, August and October-November. Hence, these months were used for the trend analyses.

4. Model assumptions

The software Visual MINTEQ (Gustafsson, 2009) employing the Stockholm Humic Model (Gustafsson, 2001) was used to study the acid-base and complexation behavior of organic matter in soils. The overall net charge (Z^-) of the soil organic matter was assumed to influence the DOC mobilization (see Introduction). At each sampling occasion, the pH value as well as the measured dissolved concentrations of ions (Ca^{2+}, Mg^{2+}, SO_4^{2-}, total Al etc.) were entered as fixed in the model, meaning that the model calculated the concentrations of solid-phase organic complexes that were in equilibrium with the given dissolved concentrations. The Z^- value can then be calculated as the sum of the charge contributions from various different organic matter species in the solid phase. As an example, in the simple case of fulvic acid and in the presence of Ca^{2+} and Al^{3+} in the soil solution, the value of Z^- would be given by:

$$Z^- = RO^- - ROCa^+ - (RO)_2Al^+ \quad (1)$$

, where RO^- is a dissociated functional group (usually a carboxylate group), $ROCa^+$ is a monodentate complex involving one functional group and one Ca^{2+} ion, whereas $(RO)_2Al^+$ is a bidentate complex involving two functional groups and one Al^{3+} ion. For more detailed information regarding the assumed complex configurations, see Gustafsson

(2001) or Gustafsson and Kleja (2005). As seen in equation 1, the value of Z^- indicates the sum of negative charge of the organic matter. Since the negative charge usually predominates, Z^- will take a positive value.

To set up the model, a number of assumptions were made:

1. The approximate organic matter content of the soil was estimated from different soil samplings carried out during the experimental period at the two sites (data not shown). Thus for the Kindla E horizon the total organic C (TOC_{soil}) content was set to 1.1 %, whereas it was 2.5 % for the Kindla B horizon, 15 % for the peat soils of the Kindla discharge area (lysimeters 6201-6203) and 1.0 % for the wet soils of the same area (lysimeters 6204-6206). In the case of the Aneboda B horizon the TOC_{soil} content was 1.5 %, for the peat soil (lysimeter 7202) 15 % and for the wet soil (lysimeters 7204-7206) 15 %. The results, however, were not sensitive to these assumptions.

2. The water content (g water / g soil) was assumed to be 1 for the peat soils and 0.1 for all other soils. Again, however, this was not crucial for the model outcome.

3. It was assumed that the fraction of "active organic matter" (AOM) amounted to 50 % of the total organic matter content in all soils. An earlier study found this figure to range between 17 and 84 %, depending on the soil, with the lowest values recorded for mor layers (Gustafsson et al., 2003). Based on these results, it can be estimated that the AOM percentage needed for the model should probably range from 30 to 84 %. However, the exact choice of the AOM percentage did not matter for the model result, and therefore an intermediate value of 50 % was chosen.

4. In the peat soils, 75 % of the AOM was assumed to consist of humic acid and 25 % of fulvic acid, whereas in other soils the percentages were 50 % and 50 %, respectively. These figures are based on an earlier detailed evaluation for different

soils (Gustafsson et al., 2003). Moreover, all dissolved organic matter (DOM) was assumed to consist of fulvic acid, to be consistent with earlier model optimizations using the SHM (Gustafsson and Kleja, 2005; Gustafsson and van Schaik, 2003).

5. Besides AOM itself, no other reactive phases in the soils were assumed to influence the net charge. This means, for example, that Fe oxyhydroxides, which could affect the net charge through adsorption of fulvic acid, were disregarded in the calculations. The reason for this is mainly that the interactions between organic matter and oxyhydroxides are very complex and still not completely understood (see e.g. Weng et al., 2007).

6. The concentration of solid-phase organic matter was assumed to be constant over the entire time period (1996-2007). Because of the large pools of soil organic matter, a change in this property over only eleven years is not expected.

7. Since the temperature was not always measured, the temperature was set to 6^{o}C for all samples. Preliminary model runs showed that the assumed value was not crucial to the model result in the pH (4-6) and temperature ranges (0-14^{o}C) investigated.

5. Results

The soil solution was highly acidic with pH<5 and negative ANC at all sites except for in the discharge area at Aneboda and in one of the riparian lysimeters (6203) at Kindla (Table 1a and 1b). In both catchments, Na^{+} was the dominating cation, while Ca^{2+} and Mg^{2+} were of the same levels and generally less than half the concentrations of Na^{+}. The Ca^{2+} and Mg^{2+} concentrations increased downslope and exhibited soil solution concentrations close to the stream levels in the riparian soils. Except for the discharge area at Aneboda, exhibiting high concentrations of Cl^{-}, SO_4^{2-} was the dominant anion in soil solution. Compared with the mineral soils, lower SO_4^{2-} concentrations were found in

the peat (Table 1b). At Aneboda, the Na^+ and Cl^- concentration balance varied between lysimeters, while all lysimeters exhibited excess Na^+ concentrations at Kindla. The DOC concentrations in soil waters were somewhat lower at Aneboda (5-9 mg l^{-1}) compared with at Kindla (4-18 mg l^{-1}), while the opposite was true for the streams, 14 compared with 4 mg l^{-1}, respectively. Both catchments had slightly higher DOC concentrations in the riparian soils compared with uphill. The same pattern was found for dissolved Fe, while the highest dissolved Al concentrations were found in dry soils with podzols (Table 1a).

Table 1

At both sites, several lysimeters experienced decreasing DOC concentrations between 1996 and 2007. At Kindla, 7 out of 15 lysimeters had statistically significant decreasing DOC trends ($p<0.05$), whereas 7 lysimeters did not have any significant change of DOC (Table 2). Only one lysimeter in the discharge area (6202) exhibited an increasing DOC trend. At Aneboda, 3 of 12 lysimeters had statistically significant decreasing DOC concentrations. No lysimeter at any site showed increasing DOC concentrations over this time period (Table 3). As an example, Figure 3 shows the DOC concentrations in the wet soils of the Kindla site for all of which the DOC concentrations decreased.

Table 2

Table 3

Figure 3

Figure 4

For individual lysimeters there was often a strong relationship between the calculated net charge of the AOM (Z^-) and DOC, indicating that Z^- is related to DOC solubility. In

Figure 4 this relation is presented for the lysimeter 6206 from the Kindla site. This relationship was statistically significant ($p<0.05$) in 11 out of 27 lysimeters.

Despite the strong relationship between Z^- and DOC, Z^- did often not decrease by time to the same extent as DOC (Table 2 and 3). In 22 out of 27 lysimeters Z^- stayed more or less constant, verified by no statistically significant ($p<0.05$) trends. Consequently and especially evident for the Kindla site (Table 2), the ratio of Z^- to DOC often displayed a change in time with increasing trends. This implies that with time, DOC solubility decreased although the net charge did not change appreciably.

Lumsdon et al. (2005) obtained evidence for an increased hydrophobicity at lower temperatures, which would have led to an increase in the Z^- to DOC ratio. However in our study there was no statistically significant relationship between the ratio of Z^- to DOC and the measured soil temperature in any of the lysimeters (data not shown), which indicates that temperature differences were unlikely to affect the observed deviations between Z^- and DOC.

The soils at the two sites are subject to recovery from acidification. Hence 15 of the 27 lysimeters display statistically significant increases in pH between 1996 and 2007 (Table 2 & 3). However, there was one lysimeter at the Aneboda site (no. 7104) that had a decreasing pH trend (Table 3). For all except 3 lysimeters in Kindla, a decrease in the ionic strength was noticed. Examples of this from the B horizon in the intermediate zone are shown in Figure 5. At Aneboda, however, only 50 % of the lysimeters displayed a significantly decreased ionic strength with time. The ionic strength was heavily dependent on SO_4^{2-}, which in many cases decreased considerably at both sites during the investigated time period, as well as on counter-ions such as Ca^{2+}, which also decreased as a result.

Figure 5

Changes in the simulated total Al pool in the soil were not expected due to the large pools involved. With Visual MINTEQ we could simulate the total amount of Al bound to active organic matter. This pool did not change during the time period except for in 6 of the lysimeters, where calculations suggested a slight increase of the modeled Al pool (Table 2 & 3).

The logarithm of the ion activity product of $Al(OH)_3(s)$ was higher than 9 in the Kindla B horizon, indicating equilibrium with respect to this phase or with imogolite-type materials (Gustafsson et al., 2001). In other lysimeters this value was lower, which might be taken as evidence that Al solubility in these soils was controlled primarily by complexation to organic matter.

Organically complexed Fe(III) in the soil was also simulated, but as the size of this pool was calculated to be < 10 % of the organically complexed Al pool in almost all cases, Fe(III) is likely to be much less significant than Al in affecting the net humic charge and DOC solubility; these results are therefore not discussed further.

6. Discussion

An objective with this study was to understand the soil water trends in DOC solubility using the Visual MINTEQ geochemical model. Since DOC solubility cannot be simulated directly, the modeled net charge Z^- was used as a proxy, using the assumption that Z^- would be directly related to DOC. For individual lysimeters there was indeed a rather strong relationship between these two variables (Figure 4). Despite this, the model-generated Z^- values indicated largely unchanged DOC concentrations for the Kindla site, whereas in reality DOC decreased in most lysimeters.

Similar results were obtained by Lofts et al. (2001), who used the WHAM model to simulate DOC solubility in soil suspensions from batch experiments using a modified version of the model of Tipping and Woof (1990). They found that for some mineral soil horizons with a comparably high Al content, the model failed to describe correctly the

DOC solubility at low pH. These data showed a minimum in the observed DOC solubility between pH 4 and 5, whereas the model indicated ever decreasing DOC with decreasing pH. Similar batch experiment results were obtained by Gustafsson et al. (2003). Figure 6 shows batch experiment results from four B horizons in which the pH dependence was varied through additions of acid or base. Similarly to some of the B horizons analyzed by Lofts et al. (2001) a minimum of the DOC concentration was observed between pH 4 and pH 5, depending on the soil.

Figure 6

Figure 7

One of the soils, Tyresta Bs, was analyzed in more detail (for the properties of this soil sample, see Gustafsson et al., 2003). By using the procedures described earlier, Z^- was calculated for the different sample points. As Figure 7 shows, the modeled Z^- did not follow the DOC curve very well, Z^- decreased with decreasing pH until pH < 4. At this point most of the bound Al dissolved, which explains the minimum in Z^- at this point. The results are consistent with the ones of Lofts et al. (2001) for the Waldstein Bw and Bs horizons.

Lofts et al. (2001) hypothesized, based on WHAM modeling, that the increased DOC at decreasing pH below pH 4 could be due to the development of positive charge on the humic colloids. However, the SHM results did not support this hypothesis since the increase in the simulated Z^- value at very low pH was caused by Al^{3+} desorption, thus leading to a slightly increased net negative charge despite the pH decrease. Interestingly to note is that the increased DOC concentrations in soil solution at the Lysina catchment in the Czech republic (Hruska et al., 2009) occurs at this low pH-interval. Unfortunately, the soil water Al^{3+} concentrations were not reported, but it could be speculated whether the positive DOC trend, besides ionic strength, was affected by an increased net negative charge on the AOM due to a changed solid-solution Al chemistry. There was no trend in pH (op.cit.).

As a result of the mismatch between DOC and Z^-, the Z^-/DOC ratio increased considerably with increasing pH between pH 4 and pH 5 (Figure 8). This mirrors the results obtained for the lysimeters, since a close inspection of the results in Table 2 and 3 reveals that the Z^-/DOC ratio usually (11 out of 15 cases) increased when the pH increased. In the one lysimeter that had a pH decrease (nr. 7104) the Z^-/DOC ratio decreased between 1996 and 2007. This suggests a consistency between the results obtained in equilibrations with soil samples on the laboratory and the lysimeters at the two sites.

Figure 8

A question that remains unanswered is what causes this deviation between Z^- and DOC. The model results do not provide any consistent clue to this. However it is clear that the pH value does seem to have an effect such that an increased pH requires a higher net charge for DOC to remain dissolved to the same extent. One possible reason could be related to the coordination of Al^{3+} in organic complexes. If a higher pH causes a higher coordination number for complexed Al^{3+}, then it follows that Al^{3+} could bridge together organic matter molecules more efficiently leading to increased aggregation. This would explain the patterns observed since cation bridging as such would not influence the Z^- value. This may not be the only possible reason, however.

Concerning factors influencing Z^-, it might be expected that an increased pH value would cause higher DOC concentrations because of increased dissociation of organic matter and hence an increasing net charge. However, other factors affecting the net charge and DOC solubility also need to be taken into account, such as changes in the ionic strength and in the soil Al pool. Figure 9 shows model-generated results for two lysimeters in which the influence of different factors were considered. The scenarios were based on observed data from 1996 and 2006 (see Table 4). An increased pH clearly increased the net humic charge as expected, but the net effect was influenced also by changes in ionic strength and total Al.

Depending on the soil, the humic charge is dependent on the net result of these different factors. At the Kindla site, Al does not change over time significantly in 13 out of 15 lysimeters (Table 2) and therefore the charge is dependent primarily on the changes in ionic strength and pH, which counteract each other to give a largely unchanged value of Z^-.

Figure 9

Table 4

Figure 9 shows that the concentration of total Al in the soil (mainly as organic complexes) was very important for the net humic charge. This was not unexpected since a larger amount of Al reduces the net charge according to equation 1. At the Aneboda site 3 of 12 lysimeters experienced significant increases in the simulated soil Al pool. The modeling results in Figure 9 show that this might have contributed to the observed decreased humic charge and hence presumably to decreased DOC concentrations. It does not seem likely that this is a "real" increase in complexed Al in the soil, because of the very large pools of Al involved. The result might reflect a change in the hydrological pathways over time, i.e. that the water that enters the lysimeter may be drained from slightly different pores. Based on the annual median water volumes collected by 6 lysimeters during the period 1994-96 (mean 338 ml) and 1998-2010 (450 ml), there are no signs of clogging in the B-horison lysimeters at Aneboda.

Based on these observations, it is evident that the well-documented recovery from acidification does not necessarily have to generate increasing DOC trends in soil solution. Depending on changes in pH, ionic strength and soil Al pools, the trends might be positive, negative or indifferent. The variation in DOC trends between lysimeters can be large within a short distance between the sampling devices and, therefore, it is necessary to have data from many sampling sites in order to assess the general DOC trends in the forested mosaic landscape. The negative DOC trends found in soil solution at many sites

in Sweden and Norway (Wu et al., 2010; Zetterberg and Löfgren, 2009) while surface waters in the same regions exhibits positive DOC trends might be explained by non-representative sampling sites, but it might also be a result of other factors as described by Clark et al. (2010). Processes in discharge areas and peatlands seem to be important landscape elements (Köhler et al., 2009; Laudon et al., 2004). Due to the high hydraulic connectivity with the streams, the explanations to the DOC-trends in Scandinavian surface waters should be searched for in such types of landscape elements.

7. Conclusions

In summary, this model exercise has highlighted the following factors of importance for the observed decrease of DOC in many lysimeters of the Aneboda and Kindla sites:

- The increased net charge following the pH increase (because of increased acid dissociation) was in many cases counteracted by a decreased ionic strength, which acted to decrease the net charge and hence the DOC solubility.

- Particularly at the Kindla site, the pH increase induced reduced solubility of DOC despite no or little change in the net humic charge, perhaps because of a change in Al coordination that increased cation bridging effects. This effect could not be verified by the model, but is supported by earlier published results from batch experiments with soil samples from B horizons.

- At the Aneboda site, an increase in the simulated concentrations of the soil Al pool from 1996 to 2007 was obtained in 3 of 12 cases; the model suggested that this might be a major reason to decreased DOC concentrations at this site. It seems unlikely that this result reflects a “real” increase in the soil Al pool. A possible reason might be differences in the hydrological pathways for the water entering the Aneboda lysimeters.

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Table 1a. Lysimeter installation information regarding hydrology, distance to the stream (ΔD), soil type, soil horizon, humus layer thickness (O-hor), depth below soil surface (ΔL), number of observations (n) and the concentrations (mean ± standard deviation) of DOC, pH, ionic strength, Al and Fe in soil water and stream water at Aneboda and Kindla during the period 1996-2007. nd = no data

Lysimeter	Hydrology*	ΔD (m)	Soil	Horizon	O-hor (cm)	ΔL (cm)	n	DOC mg/l	pH	Ionic strength mmol l^{-1}	Al µg/l	Fe µg/l
Aneboda												
7101	Rech	105	Podzol	B-hor	8	38	42	6.4±5.5	4.89±0.33	0.21±0.04	410±207	27±24
7102	Rech	101	Podzol	B-hor	8	38	42	6.1±4.3	4.59±0.11	0.56±0.15	1520±244	22±14
7103	Rech	95	Podzol	B-hor	8	38	42	7.1±5.4	4.73±0.14	0.32±0.07	870±263	17±26
7107	Rech	96	Podzol	B-hor	8	38	42	4.8±2.9	4.77±0.18	0.34±0.14	1083±400	16±13
7109	Rech	92	Podzol	B-hor	8	38	40	5.7±1.9	4.65±0.08	0.42±0.15	1184±232	29±17
7113	Rech	101	Podzol	B-hor	8	38	42	7.3±3.9	4.81±0.41	0.40±0.15	1177±346	19±9
7104	Interm	21	Podzol	B-hor	8	38	42	6.0±3.1	4.66±0.37	1.51±0.34	1874±835	20±18
7105	Interm	21	Podzol	B-hor	8	38	42	8.9±3.7	4.38±0.06	2.21±0.21	5427±881	24±18
7204	Disch	6	Gleysol	Mineral	7	37	42	5.6±6.7	4.91±0.16	0.89±0.19	1063±263	26±14
7205	Disch	5	Gleysol	Mineral	7	37	42	7.7±4.1	5.42±0.21	0.70±0.15	438±203	361±499
7206	Disch	4	Gleysol	Mineral	7	37	39	8.6±3.7	5.11±0.26	0.79±0.17	566±141	1722±1358
7202	Disch	1	Histosol	Peat	>50	37	42	25.7±8.2	5.05±0.25	0.60±0.20	681±232	4403±1557
Stream							*265*	13.6±23**	4.50±0.12	nd	1690±2699	488±274
Kindla												
6004	Rech	40	Podzol	E-hor	15	20	42	18.1±7.2	4.29±0.10	0.40±0.11	1343±328	587±2173
6104	Rech	40	Podzol	B-hor	15	45	35	6.3±3.2	4.77±0.10	0.36±0.08	1210±273	43±108
6105	Rech	40	Podzol	B-hor	15	45	40	12.6±12.0	4.46±0.42	0.42±0.21	1271±315	79±94
6106	Rech	40	Podzol	B-hor	15	45	39	5.2±2.4	4.79±0.07	0.33±0.06	1187±207	36±128
6001	Interm	21	Podzol	E-hor	8	13	42	10.8±3.8	4.41±0.13	0.38±0.08	1276±327	65±36
6002	Interm	21	Podzol	E-hor	8	13	36	7.5±3.2	4.60±0.07	0.39±0.07	1315±308	68±125
6003	Interm	21	Podzol	E-hor	8	13	42	7.0±2.3	4.60±0.05	0.34±0.07	1248±217	25±41
6101	Interm	21	Podzol	B-hor	8	38	39	6.5±3.5	4.61±0.08	0.41±0.08	1384±217	49±26
6102	Interm	21	Podzol	B-hor	8	38	36	4.6±1.6	4.67±0.09	0.42±0.07	1310±235	43±53
6103	Interm	21	Podzol	B-hor	8	38	39	3.8±1.1	4.74±0.07	0.34±0.07	1170±228	30±34
6204	Disch	7	Gleysol	Mineral	20	50	42	11.6±3.0	4.64±0.27	0.35±0.07	914±264	1035±1125
6205	Disch	8	Gleysol	Mineral	20	50	42	7.1±2.4	4.85±0.08	0.32±0.04	945±157	302±302
6206	Disch	5	Gleysol	Mineral	20	50	39	9.5±3.0	4.59±0.07	0.35±0.06	1308±224	72±117
6201	Disch	4	Histosol	Peat	>50	30	42	9.7±2.1	4.45±0.08	0.33±0.06	873±185	105±106
6202	Disch	5	Histosol	Peat	>50	30	42	12.0±2.0	4.88±0.31	0.30±0.12	948±163	529±278
6203	Disch	5	Histosol	Peat	>50	30	42	18.2±3.1	4.58±0.16	0.31±0.13	707±154	716±349
Stream							*280*	3.8±8.0**	4.58±0.14	nd	497±791	736±166

* Rech = recharge area, Interm = intermediate area, Disch = discharge area
**TOC

Table 1b. Lysimeter number and the concentrations (mean ± standard deviation) of base cations, mineral acid anions, fluoride and ANC in soil water and stream water at Aneboda and Kindla during the period 1996-2007.

Lysimeter	Ca	Mg	Na	K	SO_4	Cl	NO_3	F*	ANC
					µeq l^{-1}				
Aneboda									
7101	12±5	8±18	74±17	19±7	78±22	76±44	0.8±1.1	5.9±1.7	-31±41
7102	32±11	18±47	128±51	14±9	222±62	153±84	1.3±3.7	4.1±0.9	-154±52
7103	14±6	8±19	68±18	7±7	129±37	75±37	2±4.6	2.2±0.5	-92±26
7107	21±17	13±29	73±19	9±8	137±64	92±51	0.8±1.7	1.6±0.2	-98±59
7109	26±37	22±37	89±22	9±13	145±55	113±61	0.6±1	3±0.6	-98±31
7113	41±16	17±31	69±24	14±17	163±68	97±59	0.4±0.4	1.9±0.4	-104±57
7104	32±13	37±98	778±289	20±10	375±155	824±334	0.3±0.3	7.7±2.3	-251±121
7105	73±14	34±160	771±331	20±12	953±103	682±289	1.1±2.5	7.4±2.5	-614±105
7204	62±27	29±97	451±149	3±2	274±49	391±167	1.1±1.1	10.6±1.1	-52±88
7205	98±27	29±103	314±58	5±3	183±63	299±89	0.7±0.8	9.9±1	40±44
7206	90±30	28±101	351±77	6±3	205±87	364±103	1.2±2.8	12±3.2	-16±105
7202	96±26	31±100	243±36	9±3	114±121	264±51	1.2±2.2	6.9±0.8	79±62
Stream	96±18	88±18	223±20	13±17	153±69	187±28	2.5±4.7	5.4±1.2	78±57
Kindla									
6004	15±7	7±24	108±31	11±7	134±54	83±47	0.5±0.5	2.8±0.5	-58±66
6104	15±5	5±20	91±20	12±7	142±37	73±36	1±1.7	3.8±0.2	-77±36
6105	10±6	6±17	98±34	5±3	141±42	106±189	0.8±1	2.9±0.7	-111±186
6106	11±4	4±17	88±15	5±1	125±33	71±35	0.5±0.5	4±0.6	-77±29
6001	14±6	9±20	98±23	6±4	145±39	75±27	1.2±4.9	3.3±0.6	-85±34
6002	14±7	6±17	104±26	5±3	152±38	77±39	1±1.5	3.2±0.6	-85±30
6003	10±3	4±15	90±17	4±3	135±31	65±26	0.7±1.1	3.4±0.4	-81±29
6101	21±30	5±18	95±19	5±3	160±33	76±20	0.5±0.5	4.6±0.6	-95±42
6102	18±6	4±19	98±19	5±1	177±34	66±18	0.5±0.7	4.5±1	-107±29
6103	11±4	3±15	86±13	3±1	140±29	57±18	0.7±1.2	4±0.6	-81±30
6204	31±9	8±27	96±12	6±2	141±31	67±44	0.6±0.9	3.4±1	-48±23
6205	32±6	4±23	90±11	4±1	132±21	49±10	0.6±0.7	4.4±0.8	-33±16
6206	17±4	5±20	94±14	4±3	136±29	60±18	0.8±0.8	3.6±0.4	-62±25
6201	26±7	6±24	93±12	3±3	130±27	51±12	0.7±0.8	4.1±0.4	-36±17
6202	29±13	9±24	99±14	4±2	100±84	62±15	0.8±1	1.7±0.3	-3±36
6203	36±23	15±28	102±14	3±2	86±71	61±12	0.9±1.7	4±0.9	22±32
Stream	31±9	26±6	96±11	4±8	117±37	58±11	0.8±1.9	5.7±1.4	-19±30

*2005-2007

Table 2. Simulated results and comparisons with observed pH and DOC trends for individual lysimeters at Kindla during the years 1996-2007.

Kindla E horizon

Lysimeter no.	Mean pH	pH trend[a]	Mean DOC (mg/l)	DOC trend[a]	Mean calc. Z^- (mol/kg AOM)	Z^- trend[a]	Z^-/DOC trend	Mean calc. Al_{tot} (mol/kg AOM)	Al_{tot} trend[a]	Mean log IAP, $Al(OH)_3(s)$[b]	Ionic strength trend
6001	4.40	+	10.8	-	0.093	0	+	1.23	0	8.13	–
6002	4.61	0	7.2	0	0.065	0	0	1.58	0	8.93	–
6003	4.60	+	7.1	-	0.067	0	+	1.55	0	8.82	–
6004	4.29	0	17.8	0	0.123	0	0	0.95	0	7.60	–

Kindla B horizon

Lysimeter no.	Mean pH	pH trend[a]	Mean DOC (mg/l)	DOC trend[a]	Mean calc. Z^- (mol/kg AOM)	Z^- trend[a]	Z^-/DOC trend	Mean calc. Al_{tot} (mol/kg AOM)	Al_{tot} trend[a]	Mean log IAP, $Al(OH)_3(s)$[b]	Ionic strength trend
6101	4.61	+	6.3	-	0.065	0	+	1.59	+	8.94	–
6102	4.68	+	4.7	0	0.059	0	0	1.71	0	9.20	–
6103	4.74	+	3.8	-	0.055	0	+	1.76	0	9.33	–
6104	4.78	+	6.1	-	0.067	0	+	1.75	0	9.29	–
6106	4.79	0	5.1	0	0.060	0	0	1.79	0	9.38	0

Kindla discharge area

Lysimeter no.	Mean pH	pH trend[a]	Mean DOC (mg/l)	DOC trend[a]	Mean calc. Z^- (mol/kg AOM)	Z^- trend[a]	Z^-/DOC trend	Mean calc. Al_{tot} (mol/kg AOM)	Al_{tot} trend[a]	Mean log IAP, $Al(OH)_3(s)$[b]	Ionic strength trend
6201	4.46	0	9.7	0	0.078	0	0	0.99	0	7.92	–
6202	4.87	+	11.9	+	0.094	+	+	1.21	+	8.46	–
6203	4.57	0	18.0	0	0.146	0	–	0.56	0	7.17	0
6204	4.64	+	11.6	0	0.162	+	+	1.48	0	7.91	0
6205	4.85	+	7.0	-	0.086	0	+	1.74	+	9.14	–
6206	4.59	+	9.5	-	0.079	0	+	0.85	0	8.68	–

[a]+; Statistically significant if $p<0.05$ (Mann-Kendall); direction defined by Theil slope;
[b]; IAP, $Al(OH)_3(s)$ defined as: $\{Al^{3+}\}/\{H^+\}^3$

Table 3. Simulated results and comparisons with observed pH and DOC trends for individual lysimeters at Aneboda during the years 1996-2007.

Aneboda B horizon

Lysimeter no.	Mean pH	pH trend[a]	Mean DOC (mg/l)	DOC trend[a]	Mean calc. Z^- (mol/kg AOM)	Z^- trend[a]	Z^-/DOC trend	Mean calc. Al_{tot} (mol/kg AOM)	Al_{tot} trend[a]	Mean log IAP, $Al(OH)_3(s)$[b]	Ionic strength trend
7101	4.86	+	5.1	0	0.158	0	0	1.24	0	8.15	–
7102	4.60	+	5.9	0	0.077	0	0	1.59	0	8.90	–
7103	4.73	0	4.9	0	0.086	0	0	1.60	+	8.91	–
7104	4.60	-	5.2	-	0.082	-	-	1.71	0	9.18	0
7105	4.39	0	8.2	0	0.062	-	0	1.60	0	8.91	0
7107	4.78	+	4.6	-	0.071	0	+	1.72	0	9.19	–
7109	4.65	+	5.7	-	0.068	0	0	1.63	+	9.04	–
7113	4.73	+	7.4	0	0.095	0	0	1.57	0	8.96	–

Aneboda discharge area

Lysimeter no.	Mean pH	pH trend[a]	Mean DOC (mg/l)	DOC trend[a]	Mean calc. Z^- (mol/kg AOM)	Z^- trend[a]	Z^-/DOC trend	Mean calc. Al_{tot} (mol/kg AOM)	Al_{tot} trend[a]	Mean log IAP, $Al(OH)_3(s)$[b]	Ionic strength trend
7202	5.04	0	25.6	0	0.310	+	0	0.52	0	7.53	0
7204	4.90	0	5.0	0	0.130	0	0	0.81	0	9.39	0
7205	5.41	0	7.0	0	0.381	0	0	1.81	0	8.72	0
7206	5.16	0	8.6	0	0.324	0	+	0.98	+	8.55	0

[a]+; Statistically significant if $p<0.05$ (Mann-Kendall); direction defined by Theil slope;
[b]; IAP, $Al(OH)_3(s)$ defined as: $\{Al^{3+}\}/\{H^+\}^3$

Figure legends

Figure 1. Loction of the two Swedish IM sites Aneboda and Kindla.

Figure 2. Lysimeter transect localizations in the catchments of Kindla (left) and Aneboda (right). Black square = lysimeter plot at Aneboda, grey surface = peat land, solid black line = surface water/stream, hatched line = water divide, solid grey line = equidistance isoline above sea level (m).

Figure 3. DOC concentrations and smoothed trend lines (cubic spline, JMP 8.0.1) in three lysimeters (6204-6206) at the Kindla site between 1996 and 2007.

Figure 4. The relationship between DOC and the modeled net charge (Z^-) of the AOM at the Kindla site, lysimeter 6206.

Figure 5. Ionic strength (M) and smoothed trend lines (cubic spline, JMP 8.0.1) in three lysimeters (6101-6103) at Kindla (top) and in three lysimeters (7101-7103) at Aneboda (bottom) between 1996 and 2007.

Figure 6. Solubility of dissolved organic carbon (DOC) as a function of pH for four B horizons from central Sweden. Data from Gustafsson et al. (2003).

Figure 7. Solubility of dissolved organic carbon in Tyresta Bs, and the calculated Z^- value, as a function of pH.

Figure 8. The Z^-/DOC ratio as a function of pH for the Tyresta Bs soil sample.

Figure 9. Average effects of increased pH, decreased ionic strength (IS) and/or increased total Al concentrations on the net humic charge in soils. See Table 4 for model parameters.
A) Kindla, lysimeter no. 6206
B) Aneboda, lysimeter no. 7105.

Figure 1.

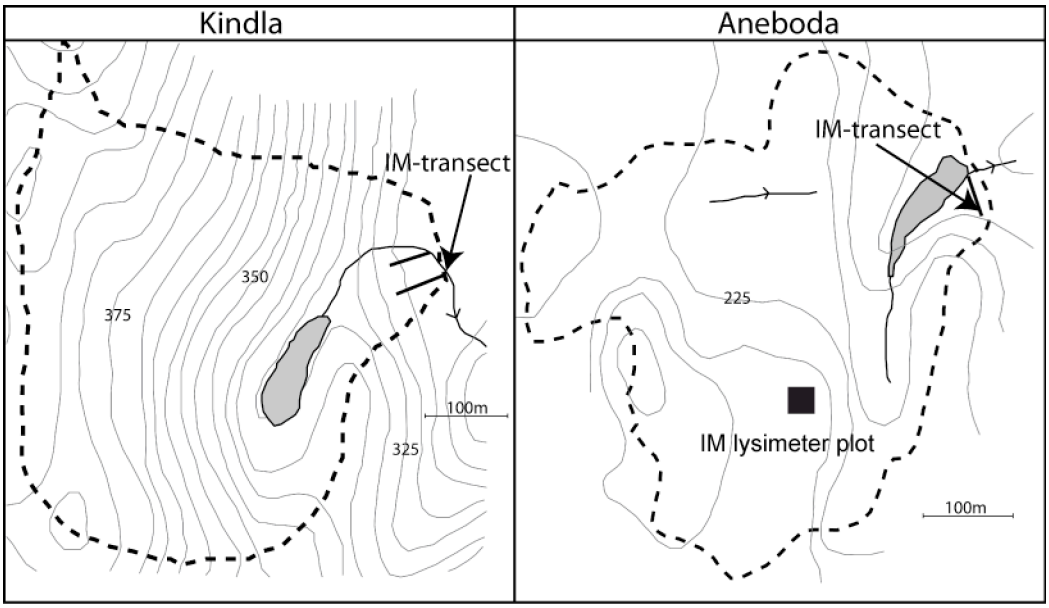

Figure 2.

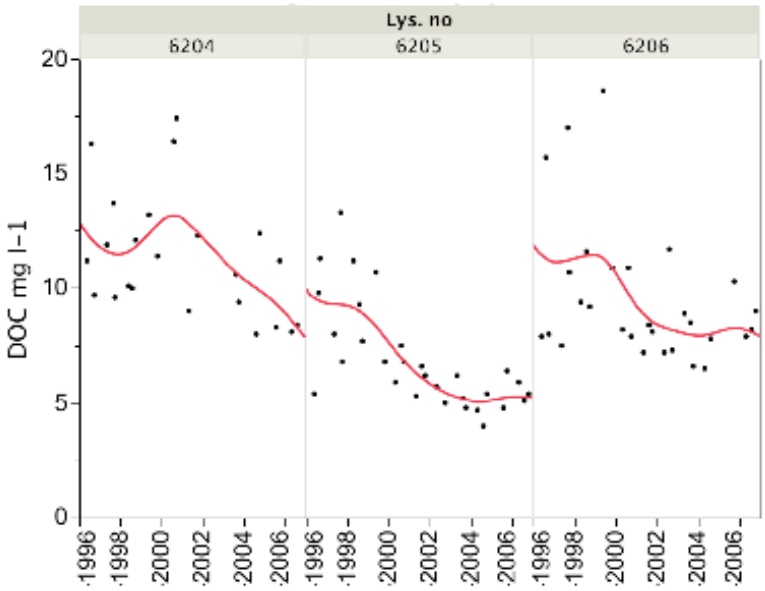

Figure 3.

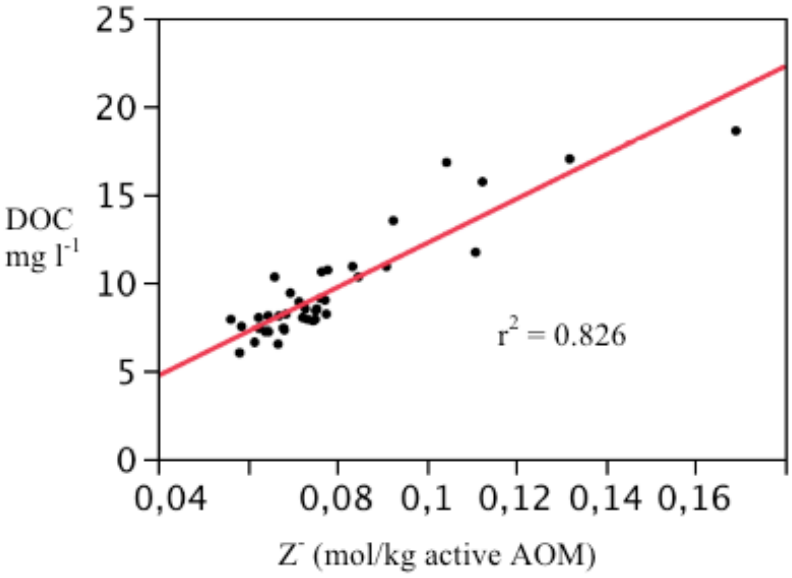

Figure 4.

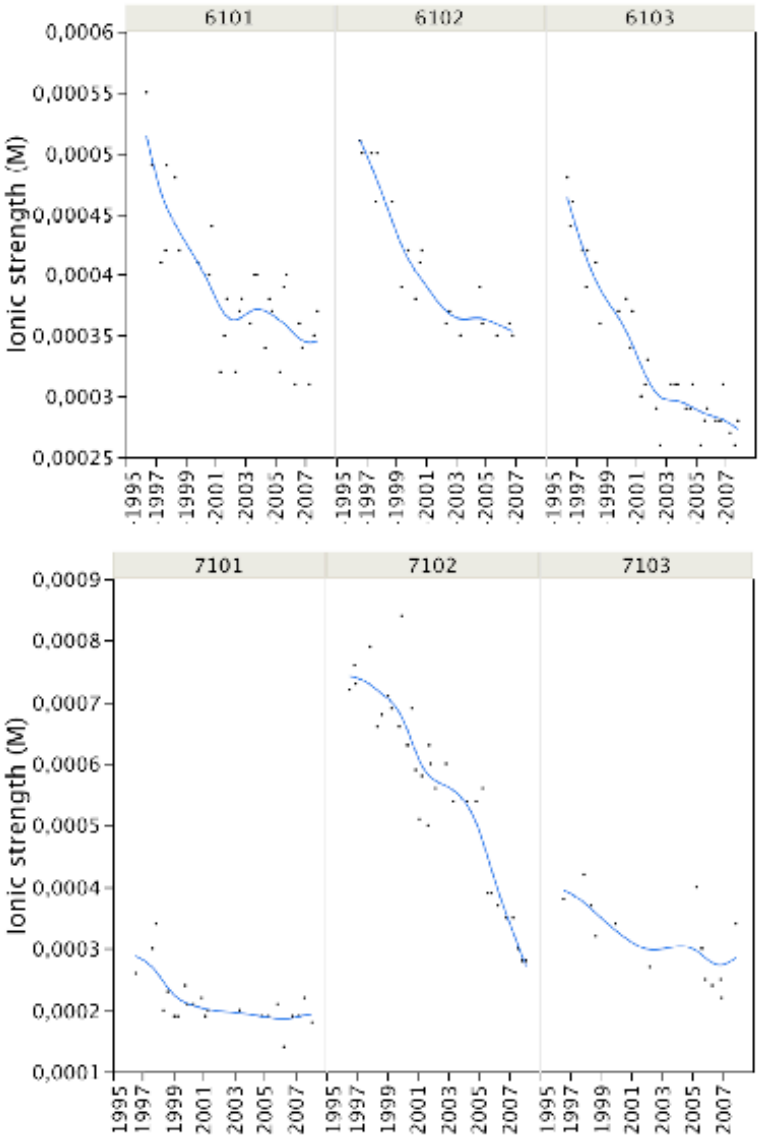
6101
6102
6103
Ionic strength (M)
0,0006
0,00055
0,0005
0,00045
0,0004
0,00035
0,0003
0,00025
1995
1997
1999
2001
2003
2005
2007
7101
7102
7103
Ionic strength (M)
0,0009
0,0008
0,0007
0,0006
0,0005
0,0004
0,0003
0,0002
0,0001

Figure 5.

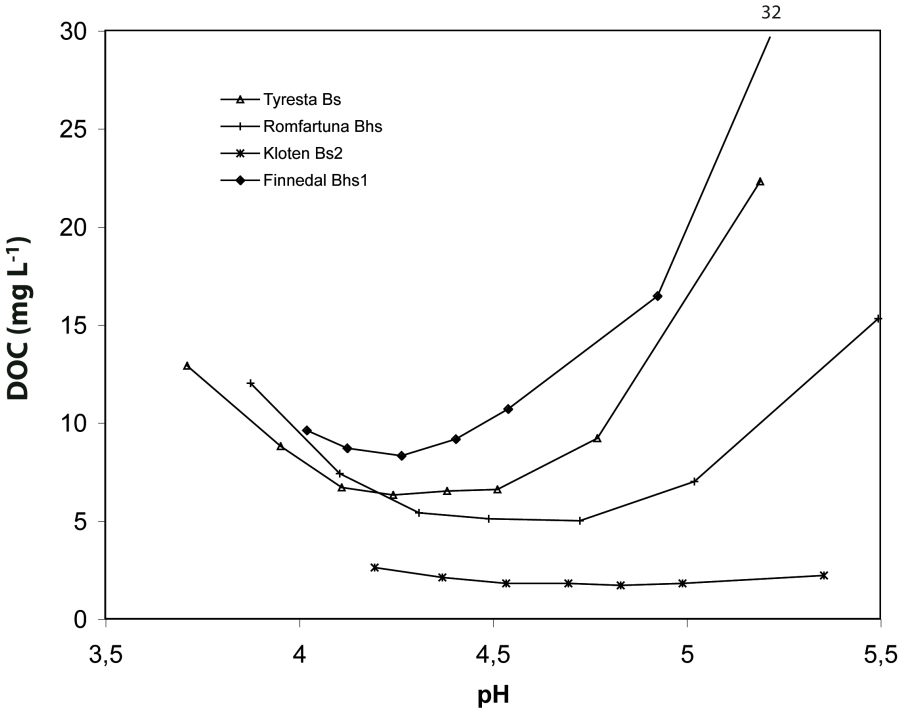
Tyresta Bs
Romfartuna Bhs
Kloten Bs2
Finnedal Bhs1
DOC (mg L-1)
pH
0
5
10
15
20
25
30
3,5
4
4,5
5
5,5

Figure 6

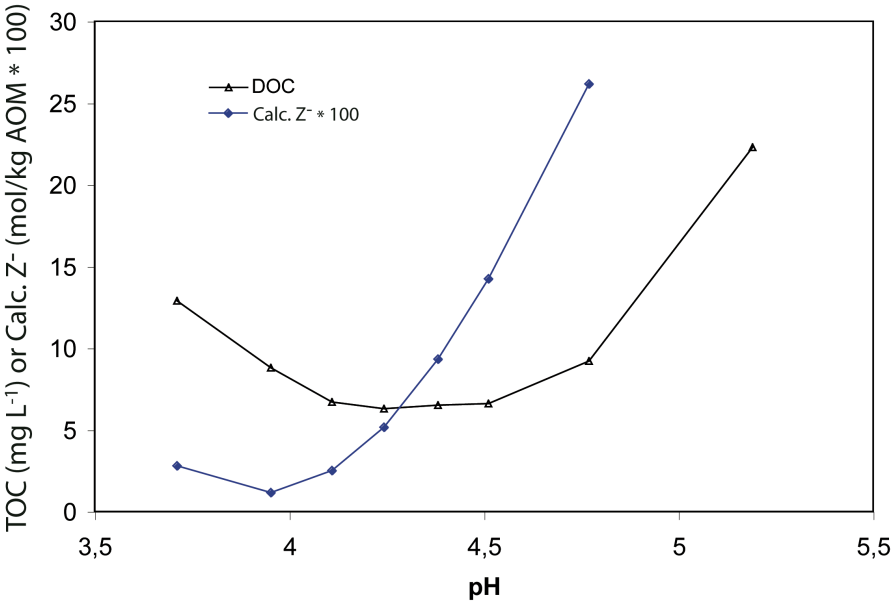

Figure 7

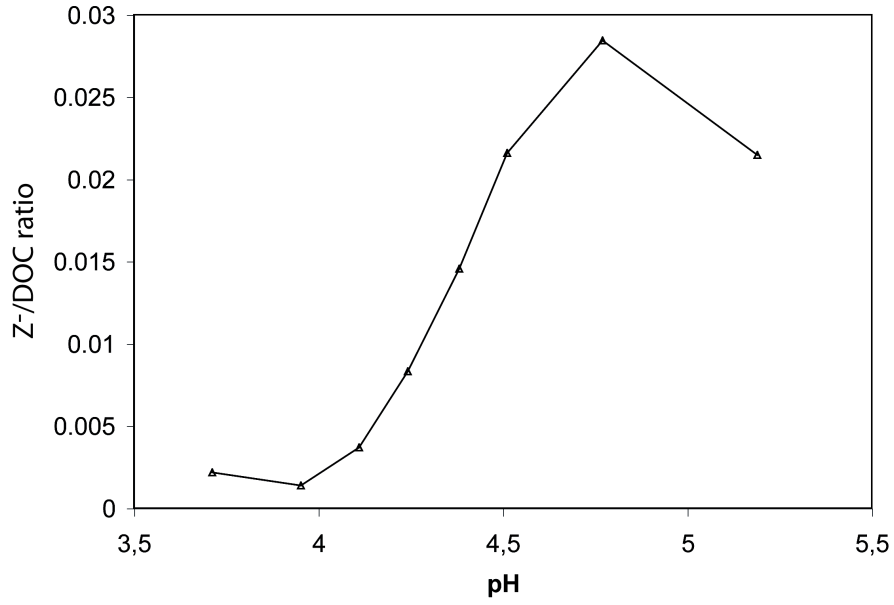

Figure 8

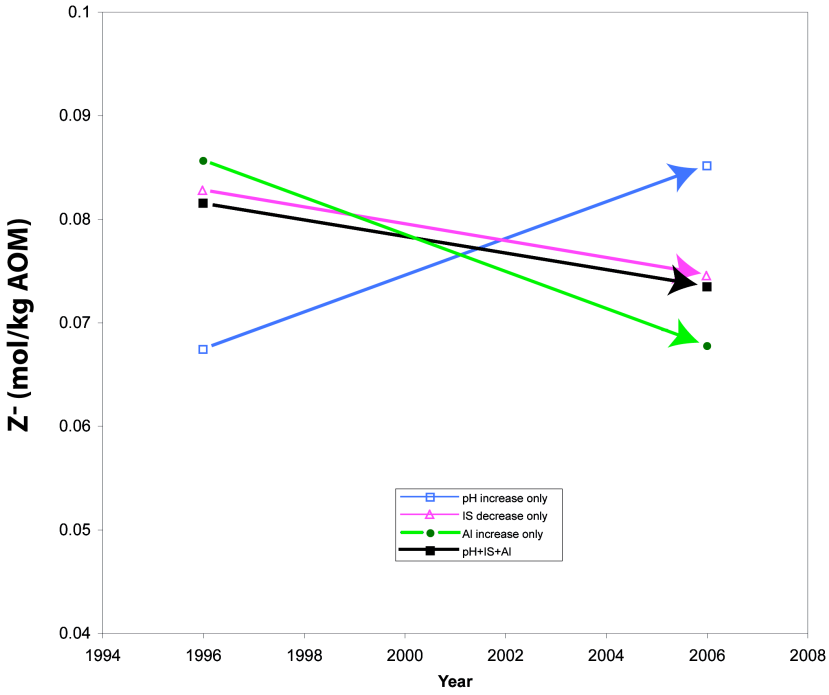

Figure 9a

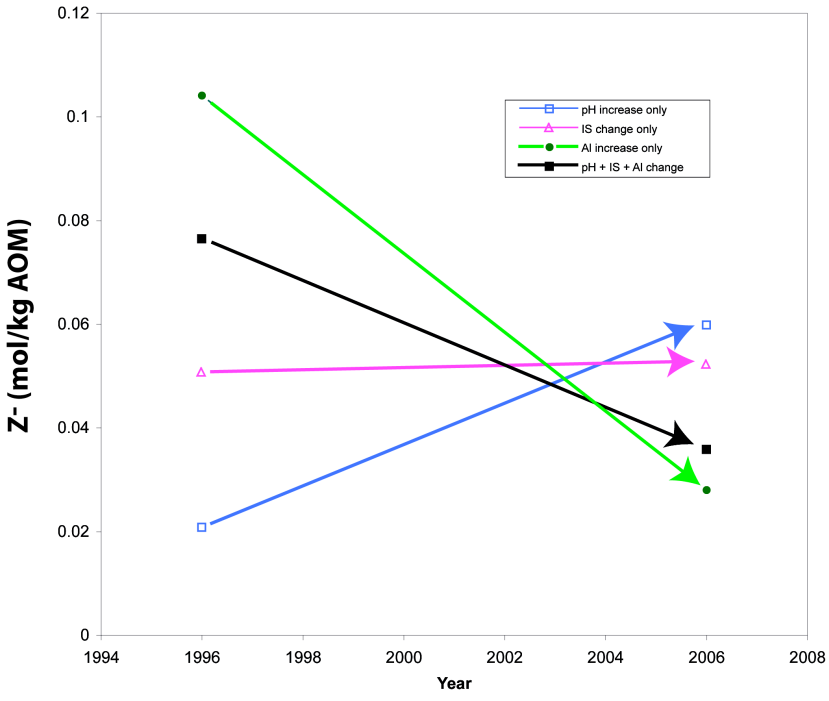

Figure 9b